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Structure of 3-bromo-4-methyl-7-ethoxycoumarin

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Abstract The title compound 3-bromo-4-methyl-7-ethoxycoumarin [$C_{12}H_{11}O_3Br$] having Br-atom at C3 belongs to the family of benzopyrones The crystal structure has been determined at room temperature Needle like crystals are monoclinic, space group $P2_1/n$ with unit cell dimensions a = 7.890(3) Å b = 12.573 (4) Å, c = 11.390(7) Å, β = 98.64(3)° and Z = 4 The structure was solved by direct method and refined by full matrix least-squares method to a final R = 0.048 for 1573 observed reflections The coumarin moiety is planar with the mean plane of the benzene ring making a dihedral angle of 2.0(3)° with the pyrone ring The Bromine atom lies in the plane of the coumarin moiety The carbethoxy group at C7 makes a dihedral angle of 7.8(4)° with the mean plane of the coumarin ring

Keywords Coumarin, X-ray crystallography

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Coumarins with various substituents at position 3 exhibit variety of biological properties [1] and are of spectroscopic interest [2]. 3-bromo-4-hydroxy-coumarin exhibits antivitamin-K property and is shown to be a monohydrate [3]. Various substituients at C4 play a vital role in the structure activity relationship studies of the induction of drug metabolising enzymes by coumarin [4] and its wide tunability in the field of dye laser [5] is interesting. Crystal structure studies of 3-bromo-khellactone-methylether [6] and dibromoeristoic [7] were useful in establishing the configuration of the respective natural products. During an attempted bromination of 4-methyl-7-ethoxycoumarin, the substitution occurred at position-3 and not at the C4 methyl group giving rise to 3-bromo-4-methyl-7-ethoxycoumarin. The position of bromine was established by the PMR spectrum which showed the absence of C3 proton around 6.5 ppm. In continuation of our crystal structure studies on 3-bromoacetylcoumarin [8] and 3-acetyl-6-bromocoumarin [9], it was though of interest to study the crystal structure of the title compound.

The title compound was synthesised by refluxing 4-methyl-7-ethoxy-coumarin (5g, 0.02ml) with N-bromo succinimide (NBS) (4.3g, 0.02ml) in 50ml of dry carbon-tetrachloride in the presence of catalytic quantity of dibenzoylperoxide for 5 hours. The reaction mixture was filtered and the filtrate was concentrated to obtain a colourless solid which was recrystallised from ethanol.

Intensity data were measured on Enraf-Nonius CAD4 diffractometer fitted with graphite-monochromatised MoK_α radiation, λ = 0.7107 Å. The crystallographic data has been tabulated in Table 1. The structure was solved by direct method and refined by full-matrix least-squares procedure based on F. Non-H atoms were refined with anisotropic thermal parameters. All hydrogen atoms have been geometrically fixed. All the scattering factors were as incorporated in NRCVAX [10] and SHELXL-97 [11] programs. The final positional and isotropic

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Table 1. Crystal data for the title compound

Crystal morphology	White
Crystal size	0.90 × 0.15 × 0.1
Chemical formula	$C_{12}H_{11}O_3Br$
Molecular weight	283.12
Crystal system	Monoclinic
Space group	$P2_1/n$
Cell constants	a = 7.890(3) Å
	b = 12.573(4) Å
	c = 11.390(7) Å
	β = 98.64(3)°
Volume	1117.1(8) Å^3
Number of formula units Z	4
Density (calculated) D_c	1.695 gm/cm^3
Absorption coefficient μ (MoK$_\alpha$)	3.67 mm^{-1}
Unique data measured	2597
Observed data with $I \geq 2.5\sigma$ (I)	1573
F(000)	568
R	0.048
R_w	0.090
Maximum electron density	0.60 e/Å^3
Minimum electron density	−0.33 e/Å^3

thermal parameters of the non-hydrogen atoms are listed in Table 2. Figure 1 shows the chemical diagram of the molecule. ORTEP [12] of the molecule with thermal ellipsoids viewed along *b*-axis is shown in Figure 2. The selected bond lengths, angles and torsion angles are tabulated in Table 3.

Table 2. The final positional and equivalent isotropic thermal parameters (Å^2) of the non-hydrogen atoms with e.s.d's in parentheses

Atom				Ueq
Br	0.3861(1)	0.1596(6)	0.1503(7)	0.0758(4)
O1	0.6997(7)	0.1557(3)	0.4695(4)	0.0638(1)
O2	0.5790(9)	0.2829(4)	0.3572(5)	0.0913(2)
O3	0.9984(6)	−0.1054(4)	0.7226(4)	0.0633(1)
C2	0.6001(9)	0.1891(6)	0.3681(7)	0.0685(2)
C3	0.5280(8)	0.1068(5)	0.2866(6)	0.0604(2)
C4	0.5604(8)	0.0014(6)	0.3041(5)	0.0577(1)
C5	0.7210(9)	0.1319(5)	0.4427(6)	0.0622(2)
C6	0.8265(1)	0.1558(5)	0.5443(6)	0.0631(2)
C7	0.8917(8)	−0.0747(5)	0.6243(5)	0.0567(1)
C8	0.8463(8)	0.0281(5)	0.5971(5)	0.0554(1)
C9	0.7382(8)	0.0496(4)	0.4919(5)	0.0541(1)
C10	0.6723(8)	−0.0289(4)	0.4114(5)	0.0537(1)
C11	1.0467(8)	−0.0253(6)	0.8100(5)	0.0594(2)
C12	1.1443(1)	−0.0779(7)	0.9178(6)	0.0755(2)
C13	0.4887(1)	−0.0834(6)	0.2198(6)	0.0717(2)

The coumarin moiety is about planar with C13, Br and O2 atoms lying in the least squares plane through C2–C10, O1 atoms. The ethoxy group at C7 makes a dihedral angle of 7.8(4)° with

Table 3. The selected bond lengths (Å), angles (°) and torsion angles of the molecule

Bond lengths

	Length		Length		Length
Br-C3	1.893(6)	O1-C2	1.362(9)	O1-C9	1.383(7)
O3-C7	1.352(8)	O3-C11	1.427(8)	C2-O2	1.195(10)
C11-C12	1.501(10)	C13-C4	1.488(9)		

Bond Angles

	Angle		Angle		Angle
C2-O1-C9	122.4(5)	C7-O3-C11	116.4(5)		
-	-	O2-C2-O1	116.5(7)	O2-C2-C3	127.1(7)
O1-C2-C3	116.4(6)	-	-	-	
O3-C11-C12	108.0(6)	-	-	O1-C9-C10	120.8(5)

Torsion angles

	Torsion angle		Torsion angle
C11-O3-C7-C8	8.8(9)	-	
-	-	C9-O1-C2-C3	3.2(1)
O1-C2-C3-C4	−2.9(1)	O2-C2-C3-Br	0.1(1)
C2-O1-C9-C10	−1.5(1)	-	
		C4-C10-C9-O1	0.9(1)
		Br-C3-C4-C13	0.3(1)

the coumarin mean plane. The dihedral angle between the benzene and pyrone ring is 2.0(3)°.

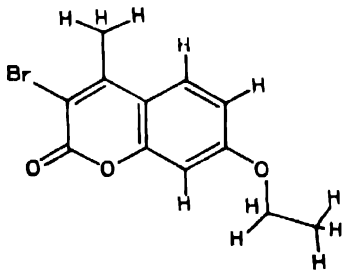

Figure 1. Chemical diagram of the molecule

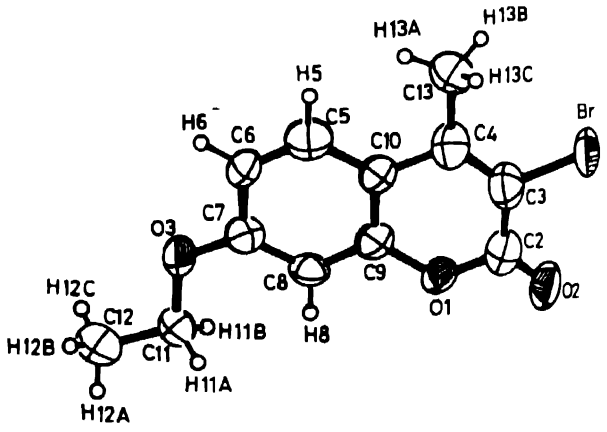

Figure 2. ORTEP plot of the molecule with thermal ellipsoids viewed along *b*-axis.

The bonds C2-O2 1.195(1) Å and C3-C4 1.358(5) Å of the pyrone ring show distinctly double bond character [13]. The bonds C2-C3 1.448(7) Å and C4-C10 1.447(4) Å adjacent to the double bond are systematically longer than 1.40 Å [13,14]. It is interesting to note the increased bond length of C3-Br 1.893(6) Å and the shortening of C2-O2 1.195(1) Å which facilitates the minimization of dipole-dipole repulsion. Also O2-C2-O1 116.5(7)° is smaller than O2-C2-C3 127.1(7)° which may result from the steric effect of the substituent at C2 and C3.

The bond angles around C2 are 116.5(7)°, 116.4(6)° and 127.1(7)° which compare with 119.9(7)°, 112.8(7)° and 127.4(7)° respectively of coumarin [9] and resemble the geometry of a carboxylic group.

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